FINAL TECHNICAL REPORT

1 JUL 91 to 30 JUN 95

The In Situ Observation of Epitaxial Diamond Thin Film Nucleation and Growth Using Emission Electron Microscopy

Submitted by

Martin E. Kordesch
Associate Professor of Physics
Ohio University, Athens, Ohio
Tel.: (614) 593 - 1703, FAX: - 0433
electronic mail: kordesch@helios.phy.ohiou.edu

Grant No. N00014-91-J-1596
R&T Number: s400028ssr02

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	27-JUN-95	Final: 1-JUL-91 to 30-JUN-95

4. TITLE AND SUBTITLE
The In Situ Observation of Epitaxial Diamond Thin Film Nucleation and Growth Using Emission Electron Microscopy

5. FUNDING NUMBERS
N00014-91-J-1596

6. AUTHOR(S)
Martin E. Kordesch

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Physics
Ohio University
Athens, OH 45701-2979
Claire Carlson, Administrative contact

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Max N. Yoder
Office of Naval Research, ONR-312
800 N Quincy St.
Arlington VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A summary of work performed under this grant is given, including publications, degrees granted, presentations and awards. Nucleation and growth of diamond, diamond heteroepitaxy on Mo(310) and Si(310), electron emission from cvd diamond, Low energy electron microscopy, synchrotron radiation based emission microscopy and molecular beam growth methods are discussed.

14. SUBJECT TERMS
emission microscopy, field emission, nucleation
CVD diamond

15. NUMBER OF PAGES
10

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

CONTENTS

page

1.0 Summary of Results

1.1 Diamond Nucleation and Growth

Two techniques for nucleation and growth studies were developed in this work, ex situ growth and transfer into the analysis chamber without exposure to atmosphere (Wang, Ph.D. Dissertation 1993), and an effusive doser for in situ growth (Garcia, Ph.D. Dissertation 1994).

The first method, described in several reports and publications (Wang et al., Ultramicroscopy 1991; Diamond and Related Materials 1994) showed that diamond could be observed on molybdenum and silicon substrates in photoelectron emission microcopy. In situ adsorption and thermal desorption effects, as well as substrate cleaning and conversion to carbide was observed and confirmed with x-ray diffraction and x-ray photoelectron spectroscopy. Diamond dissolution into the substrate at high temperature was observed on Mo. Mo carbide was found to act as a carbon diffusion barrier, and therefore indirectly enhances nucleation. Nucleation on pure molybdenum carbide was insignificant.

The second method resulted in the observation of two-dimensional carbon reaction diffusion fronts on Mo(100) and Mo(310) (Garcia et al. Applied Physics Letters 1992; JVST 1995). The possibilities for a "step-flow" mechanism for heteroepitaxy of diamond on molybdenum or silicon was proposed and investigated as a result.

1.2 Diamond Epitaxial Growth on Mo(310) and Si(310)

The two dimensional growth and stabilization by sulphur of carbon monolayers on molybdenum surfaces at temperatures used for diamond growth are detailed in the Ph.D. Dissertation by Garcia, and Garcia and Kordesch JVST A13 (1995) 1396.

Both Mo(310) and Si(310) surfaces were obtained, and an attempt to characterize these clean surfaces was made.

The Si(310) surface was not stable after extended experimentation with cleaning methods recommended by specialists. A 4-fold reconstruction was observed on a surface that ideally would have only 2-fold symmetry. An undetermined facet geometry was obtained rather than a regular step-terrace surface that could be expected to yield step-flow heteroepitaxy of diamond. Initial carbon deposition during CVD growth would also certainly alter the "clean" Si(310) surface. Diamond CVD on a Si(310) wafer prepared by the best available methods did not result in oriented growth, and showed exceptionally poor nucleation densities, as would be expected from smooth, unscratched silicon. This study was abandoned as impractical.

The BCC Mo(310) surface is very different from Si(310). The Mo(310) single crystal was used to further investigate the propagation of two dimensional reaction diffusion fronts during carbon CVD. Scanning Auger analysis indicated that sulphur was

present with the carbon deposit, and absent from the oxygen covered side of the propagation front (Garcia 1994, 1995).

Am attempt to simulate sulfur diffusion out of the Mo(310) surface using hydrogen sulfide was unsuccessful. The stabilization mechanism is therefore most likely dynamic. The implications for diamond nucleation and epitaxy may be pervasive, if, for example, sulfur stabilization is the reason for the high nucleation rate of diamond on Mo, where sulfur is always present, and segregates to the surface during diamond growth.

1.3 Field Emission from CVD Diamond

Field emission from CVD diamond films in the "diode" geometry was first reported in Wang et al. Electronics Letters, 1991. A patent was applied for on this process, but was later abandoned due to publication as an APS Abstract more than one year prior to filing the claim.

Early efforts were concerned with the "negative electron affinity" of the diamond surface, and the identification of n-type diamond. The "Latham" model of multiple field emitters at both the substrate-film and film-vacuum interface, with conductive particles for electron transport over the thick insulating diamond film was proposed to account for electron emission at sizable currents and low fields. Subsequent measurements (Shovlin 1994, 1995) have shown that the negative electron affinity is irrelevant to emission from CVD diamond, and that a combination of Latham-like injection of electrons into the diamond conduction band and ballistic transport may account for all of the experimental data on electron field emission from diamond (Kordesch 1996, in press).

1.2 Synchrotron Radiation Studies of Diamond

During January 1993, an attempt to find a negative electron affinity (NEA) signature in photoemission from diamond was made at the Wisconsin Synchrotron Center in Stoughton, Wisc. PEEM images were recorded simultaneously with electron yield spectra over the 4 to 18 eV incident photon energy range. The PEEM/VUV-yield spectra would be ideal for the detection of emission sites on NEA surfaces, since the photon energy could be scanned through the emission threshold while extracting electrons from the surface using the accelerating field of the microscope objective. Results are given in Shovlin et al. JVST 1995. This work was also supported by a NATO grant.

1.3 Low Energy Electron Microscopy

The Ohio University LEEM is fully functional as a PEEM and as a LEEM, but suffers from poor incident electron intensity in the LEEM mode. Several attempts to acquire a commercial electron

gun for high intensity electron illumination were made, some are still pending.

LEEM of the diamond (100) surface reconstruction has been hampered to date, because of a high secondary electron emission yield at the LEEM energies of a few eV, so that the secondary electron intensity is many times that of the elastic scattering intensity used for LEEM imaging. The 1X1 to 2X1 surface reconstruction has been observed as a function of temperature and consequent H desorption in the diffraction mode. A B-doped (100) diamond has been purchased as is in use to examine ways to reduce the secondary yield and permit LEEM imaging.

The LEEM instrument has been used in emission mode for testing field emitters from our and other's laboratories.

1.4 Molecular Beam Deposition

A fast ion gauge, pulsed inlet valve and a Roots blower have just been purchased to enhance the ongoing skimmer and nozzle development on the molecular beam apparatus.

Tests with 1% Argon in hydrogen were undertaken, but no conclusive results are available, since some questions about the alignment of the skimmer to nozzle accuracy remain. In the one test so far, no kinetic emission was observed with either 1% methane in hydrogen or 1% Argon in hydrogen. A simpler design, with greatly reduced skimmer to surface distances is now in the construction phase.

Investigation of Iodomethane and similar compounds was suspended due to their toxicity. Their investigation will be postponed until proper safety measures can be instituted.

1.5 Thermal Emission Microscopy of Molten Cu and Barium Activated Emitters.

An undergraduate project to observe the segregation of carbon to the surface in molten Cu was completed. The observation of molten copper was not practical, since evaporation of the metal proceeded at a very high rate during observation. Manganese was chosen as a substitute, and excellent images of a dynamic melting and evaporation process, with distinct boundaries at the propagation front were observed. A short discussion is contained in the invited paper (Kordesch, JVST 1995).

A second thermal emission microscopy study was undertaken by an undergraduate. In this work, barium carbonate was heated in situ on a CVD diamond substrate, and the threshold for field emission determined after conversion of the barium to Ba metal and Ba carbide. The threshold was reduced over 200 K, indicating a reduced work function. No enhancement of the low field cold electron filed emission was observed, further confirming the Latham model for electron emission, and the irrelevance of the negative electron affinity of diamond in this process.

2.0 Reports/Publications/Presentations

Reports:

1. Semiannual Technical Report: 1/7/91-1/3/92
2. Semiannual Technical Report: 1/4/92-31/12/92
3. Semiannual Technical Report: 1/1/93-30/6/93
4. Semiannual Technical Report: 1/7/93-31/12/93
5. Semiannual Technical Report: 1/1/94-30/6/94
6. Semiannual Technical Report: 1/7/94-30/6/95
7. Final Technical Report: 1/7/91-30/6/95

Papers Published:

1. "An Emission Microscopy Study of Carbon Surface and Thin Film Morphology," C. Wang and M.E. Kordesch, Ultramicroscopy, 36 (1991) 154-163.

2. "An UHV Photoemission Microscope for use in Surface Science," W. Engel, M.E. Kordesch, H.H. Rotermund, S. Kubala and A.van Oertzen, Ultramicroscopy, 36 (1991) 148-153.

3. "Cold Field-Emission from CVD Diamond Films Observed in Emission Electron Microscopy," C. Wang, A. Garcia, D.C. Ingram, M. Lake and M.E. Kordesch, Electronics Letters 27 (1991) 1459-1461.

4. "A Sample Tilting Mechanism and Transfer System for High-Temperature Thin Film Deposition and UHV Electron Microscopy," Adrian Garcia and Martin E. Kordesch, J. Vac. Sci. Technol., A11 (1993) 461.

5. "The Controlled Deposition and Lateral Growth of an Ordered Carbon Layer on Mo(100) Observed In Situ," Applied Physics Letters, 61 (1992) 2984.

6. "Electron Emission Microscopy for In Situ Studies of Diamond Surfaces and CVD Diamond Nucleation and Growth", Martin E. Kordesch, Proceedings of the 3rd International Symposium on Diamond Materials, K.Spear, J. Dismukes and K.Ravi eds., The Electrochemical Society, Pennington NJ, 1993, 787. Invited Review.

7. "An In Situ Observation of CVD Diamond Etching and Dissolution Using Photoelectron Emission Microscopy," C. Wang, J.Macaulay, J.D. Shovlin and M.E. Kordesch, Diamond and Related Materials, 3 (1994) 1066-71.

8. "Electron Emission from Chemical Vapor Deposited Diamond and Dielectric Breakdown", J.D. Shovlin and M.E. Kordesch, Appl.Phys.Lett. 65 (1994) 863.

9. "Removal of Non-Diamond Carbon from CVD Diamond Surfaces", W. Engel, D.C. Ingram, J. Keay and M.E. Kordesch, Diamond and Related Materials, 3 (1994) 1227-9.

10. "Photoelectron Emission Microscopy", M.E. Kordesch, CRC Handbook of Surface Imaging and Visualization, A.T. Hubbard, ed., Boca Raton, 1995. Book Chapter.

11. "Surface Reaction Diffusion Fronts Observed with Photoelectron Emission Microscopy During Carbon Deposition on Mo(310)", Adrian Garcia and Martin E. Kordesch, J. Vac. Sci. Technol., A13 (1995) 1396.

12. "Synchrotron Radiation Photoelectron Emission Microscopy of Chemical Vapor Deposited and Natural Diamond Surfaces" J.D. Shovlin, M.E. Kordesch, D. Dunham, B.P. Tonner and W. Engel, J. Vac. Sci. Technol., A13 (1995) 1111.

13. "Probing Reactive Deposition and Surface Dynamics using Real-time Emission Microscopy", Martin E. Kordesch, J.Vac. Sci. Technol., A13 (1995) 1517. Invited Review.

14. "Buckytube Cold Field Emitter Array Cathode Experiments" B.H. Fishbine, C.J. Miglionico, K.E. Hackett, K.J. Hendricks, X.K. Wang, R.P.H. Chang, J.D. Shovlin and M.E. Kordesch, Proc. Matl.Res. Soc. 359 (1995) 93-98.

In Press:

15. "Electron Emission from Natural and Chemical Vapor Deposited Diamond Observed with Emission Microscopy", J.Vac.Sci. Technol., Invited Review.

16. "In Situ Real Time Emission Microscopy Applied to Chemical Vapor Deposition of Diamond And Nitrides, Proc. Matl. Res. Soc., Invited Review.

17. "An Emission Microscopy Study of Chemical Vapor Deposited Aluminum Nitride Films", Proc. Matl. Res.Soc., Boston, 1995.

American Physical Society Abstracts:

1. Bull.Amer.Phys.Soc., 40 (1995) 321.
2. Bull.Amer.Phys.Soc., 40 (1995) 480.
3. Bull.Amer.Phys.Soc., 39 (1994) 653.
4. Bull.Amer.Phys.Soc., 39 (1994) 161.
5. Bull.Amer.Phys.Soc., 36 (1991) 344.
6. Bull.Amer.Phys.Soc., 36 (1991) 646.

Invited Lectures/Colloquia/Seminars:

1991 "Surface Chemistry of the Isoelectronic Trio: NO+, CO, CN"
- University of Vermont, Burlington, Chemistry Dept.
"Vibrational Spectroscopy of H adsorbed on Pt, Pd and Rh "
- Condensed Matter and Surface Science Seminar, Ohio U.

1992 "Low Field Cold Emission From CVD Diamond Films"
- DARPA Contractors Meeting, MIT Lincoln Labs.
- Condensed Matter and Surface Science Seminar, Ohio U.
"Emission Microscopy of Surfaces and Thin Films"
- Ohio University, Physics Dept. Colloquium

1993 "Electron Emission Microscopy for In Situ Studies of Diamond Surfaces and CVD Diamond Nucleation and Growth"
- University of Illinois at Chicago Circle.
- 3rd International Diamond Symposium, The Electrochemical Society, Honolulu.
- Fritz Haber Institute d. MPG, Berlin
"Photoelectron Emission Microscopy"
- Tutorial Lecture, Microscope Society of America.

1994 "Supersonic Molecular Beam Growth of Diamond"
-Gordon Research Conference, Diamond Synthesis.
"Probing Reactive Deposition and Surface Dynamics Using Real Time In Situ Emission Microscopy"
- 41st National Symposium of the American Vacuum Society, Denver.

1995 "Emission Microscopy of Natural and CVD Diamond Field Emitters"
- 6th Diamond Technology Workshop, Detroit.
- 42nd National Symposium of the American Vacuum Society, Minneapolis.
"In Situ Photoelectron Emission Microscopy of Diamond and Nitride Surfaces"
- Materials Research Society Fall Symposium, Boston.
- Fritz Haber Institute d. MPG, Berlin.
"Photoelectron Emission Microscopy"
-Invited Instructor, 2nd Nicolas Cabrera Summer School, Madrid.

3.0 Degrees Awarded:

Bachelor of Science in Physics with Honors, Honors Thesis

1. Mark Little, 1995 Honors Thesis: "Barium assisted Thermal Emission Microscopy of CVD Diamond Films"

2. Julie Beegan, 1995 Honors Thesis: "Transmission Electron Microscopy of Chemical Vapor Deposited Diamond"

3. Stephen Pellathy, 1994 Honors Thesis: Thermal Emission Microscopy of Molten Manganese"

4. Tina McNett, 1994 Honors Degree in BOTH Chemistry and Physics, "Bonding of Phosphors for Phosphor Screens"

Bachelor of Science, Senior Project:

5. Robert Arts, B.S. Physics 1991, Raman Spectroscopy of CVD Diamond Films"

Masters of Science:

6. Li Wu, Project: "X-ray diffraction analysis of Carbon Fiber Composites".

7. Bert Whittaker III, Thesis: "The feasibility of CVD Diamond Growth on Epitaxial Iron Films".

8. Myungsoo Kim, Project: "Diamond Growth at High Temperatures using Carbon Tetrachloride".

9. Baki Altuncivahir, Thesis: "Vacuum System for a Supersonic Jet Molecular Beam Deposition System".

Doctoral of Philosophy:

10. Congjun Wang, Ph.D. 1993, Dissertation: "A Photoelectron Emission Microscope Study of CVD Diamond Films and Diamond Nucleation".

11. Adrian Garcia, Ph.D. 1994, Dissertation: "Two-Dimensional Growth Fronts Observed on Molybdenum Surfaces".

12. Joseph D. Shovlin, Ph.D. expected 1996: "Electron Emission Microscopy of Diamond and Nitride Field Emitters"

13. Vincent Ballarotto, Ph.D. expected 1998: "Supersonic Molecular Beam Growth and Emission Microscopy of Diamond and Nitrides".

4.0 Awards and Honors:

In addition to the honors graduates and scholarship holders supported on this grant who worked on diamond related theses and projects, formal awards were:

1. Promotion to Associate Professor and tenure, to Dr. Kordesch, 1993.
2. Honors Tutorial College Internship, to Dr. Kordesch
3. Jeannette Grasselli Undergraduate Research Award, 1994-5, to Julie Beegan, for research on CVD Diamond.